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The emission of secondary clusters and its relevance for analytical Laser-SNMS

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Summary. The emission of secondary dimers and trimers under 8 keV Ar^+ ion bombardment has been investigated under the aspects of its relevance for quantitative SNMS analysis and its implication for the basic understanding of the sputtering process. The measurements have been performed with a newly developed Laser-Multiphoton-Ionization-TOF-SNMS apparatus. The problematic of saturation and fragmentation of multimers in Laser-SNMS is addressed and compared for different ionization techniques. Cu and Cr metal as well as a CuAgAu alloy with known element concentrations have been investigated using 308 and 193 nm laser radiation for post-ionization. The data imply, that for these materials and primary ion energies dimer/atoms ratios of 10–30% are characteristic. These numbers also imply, that neglecting cluster-contributions can lead to substantial errors in quantitative analysis.

I Introduction

If a clean metal is bombarded with inert gas ions, it is well known that the sputtered flux consists mainly of neutral monoatomic target particles [1]. In general, only a small fraction of the sputtered flux is assumed to consist of secondary molecules, dimers and trimers. However, the relevance of secondary dimers and trimers is still an open question and different numbers for the *Secondary Cluster/Secondary Atoms* ratios are reported in the literature [2–6]. Furthermore, the mechanisms for cluster emission are still not resolved in all details and different models have to be considered [7–9].

The essential question relevant for quantitative analysis methods based on the detection of secondary particles, which is addressed in this context, however, is the amount of neutral clusters in the total secondary flux. In fact, in most practical applications the concentration of one particular target component is assumed to be proportional to the SIMS or SNMS signal of the element. In principle, the corresponding cluster or molecular contributions could be monitored together with the elemental signals. However, this makes the analysis more complicated. But much more severe complications and limitations can arise from the fact, that the clusters simply cannot be "registered" because of various reasons. The most probable cause for this, if using methods employing post-ionization of neutrals, is fragmentation of clusters (and molecules). As an additional complication, the amount of fragmentation will differ for various clusters and it will depend on the intensity of the ionizing radiation.

A typical "situation" encountered in Laser-SNMS investigations of clusters is shown in Fig. 1. The amount of cluster-photo-ions detected is plotted against the arbitrary power P of the ionizing laser radiation. In general, two or three photons are needed to ionize the neutral secondaries, atoms as well as clusters. Therefore, as indicated in region I in the figure a P^n (n = 2, 3) dependence on the laser power for the signal will be observed for low radiation intensities according to the theory of non-resonant multiphoton ionization [10]. At sufficiently high laser powers the signal will eventually saturate. This case is represented in region III of the figure. So far the statements are valid for all kinds of

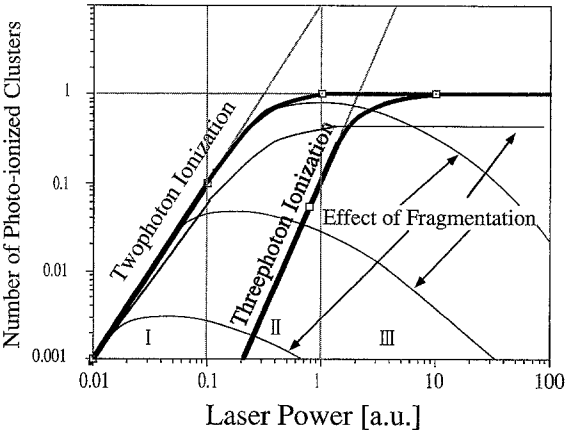

Fig. 1. Schematic representation of the cluster-photo-ion signal in a Laser-SNMS experiment. The cluster signal as a function of the laser power can be represented as a sum of two power dependent cross sections: a) the ionization cross section and b) the fragmentation cross section which itself is a complex sum of contributions from different fragmentation channels. Possible cases are shown in the figure

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secondaries. As long as only monomers are measured, this regime is optimal for quantitative analysis, because it corresponds to an ionization probability of one, independent of laser power fluctuations. For clusters, however, this is not necessarily true anymore. In this case the situation is more complex and the optimal laser power regime has to be chosen according to the intentions of the investigation. Region II represents a transition from the P^n dependence to saturation. The fragmentation of clusters and molecules, as will be shown later, will be a function of the laser-power and can cause a drop in the cluster-photo-ion signal for high laser powers. The amount of fragmentation at a given laser power can range from negligible to 100% fragmentation depending on the electronic structure of the clusters and the wavelength of the ionizing radiation. In principle, several possible channels for fragmentation can be operative, involving single or multiphoton process. The cluster-photo-ion signal, therefore, as a function of the flux will exhibit one of the shapes shown in Fig. 1. In particular, if fragmentation is only due to two-photon processes (same order as the ionization, i.e. dissociative ionization $Me_2 + 2\,hv \rightarrow Me^+ + Me + e^-$) saturation at a reduced signal level should be observed. In many cases, however, we have noticed a reduction of the multimer signal with increasing laser flux, indicating fragmentation processes involving a different number of photons.

Assuming that the signal of the atomic photo-ions behaves like the ionization curve in Fig. 1 and that the corresponding cluster-photo-ions can be described by one of the fragmentation curves, then the measured *Clusters/Atoms* ratios will strongly depend on the laser power and the laser wavelength. Furthermore, it should be mentioned, that the ionization cross sections of clusters, as compared to atoms, are generally higher, because the chance of intermediate quasi-resonance levels is considerably higher.

Let us recall that Fig. 1 presents the situation for postionization by an intense laser radiation via multiphoton ionization. Similar arguments will apply for other ionization methods as well. However, most other ionization methods will not easily achieve saturation of the ionization process. It is, therefore, not astonishing that the *Clusters/Atoms* ratios for secondaries obtained by different groups for various elements and ionization methods differ quite substantially and range from well below 10^{-2} up to 4×10^{-1} [3–5].

In this paper we present detailed investigations of the neutral cluster yield for Cu, Ag and Au, for which very high cluster contributions have been reported and compare it with the corresponding yield for Cr, where low cluster yields are found in the literature [4]. The use of two different laser wavelengths (308 und 193 nm) for post-ionization will allow us to obtain a better estimation of the *Clusters/Atoms* ratios and the related physics. With these data we will take a closer look at the relevance of cluster emission during ion bombardment for quantitative analysis, in particular using Laser-SNMS.

II SNMS spectrometer and experimental

The cluster yield studies were performed under UHV conditions (2×10^{-10} mbar base pressure) using a newly developed SNMS/SIMS instrument, which is shown in Fig. 2. A detailed description of the instrument can be found in [11]. In this device Time-of-Flight (ToF) mass spectrometry can be performed of either photo-ionized sputtered/desorbed neutral atoms and molecules by intense laser radiation, or direct analysis of the secondary ions. In SNMS mode the atoms and molecules sputtered by the probe beam are ionized by non-resonant laser multiphoton ionization (MPI) [12, 13]. The photo-ions are accelerated into a high resolution ($m/\Delta m = 1000$), high transmission time-of-flight mass spectrometer of the reflecting type [14] and detected by a chevron microchannel plate assembly. In this mode the detection efficiency is $\approx 10^{-4}$. Any secondary ions formed are electrostatically suppressed in the SNMS mode. Time-of-flight mass spectrometry has the big advantage that all masses are recorded quasi-simultaneous. A Lambda Physik excimer laser operated with XeCl or ArF (wavelength of 308 and 193 nm) was used for photo ionization. The analysis was performed with a 8 keV Ar^+ beam with up to 2 μA current and a beam diameter of 3 mm provided from a Colutron ion source. The ion gun axis is tilted 45° from the target normal.

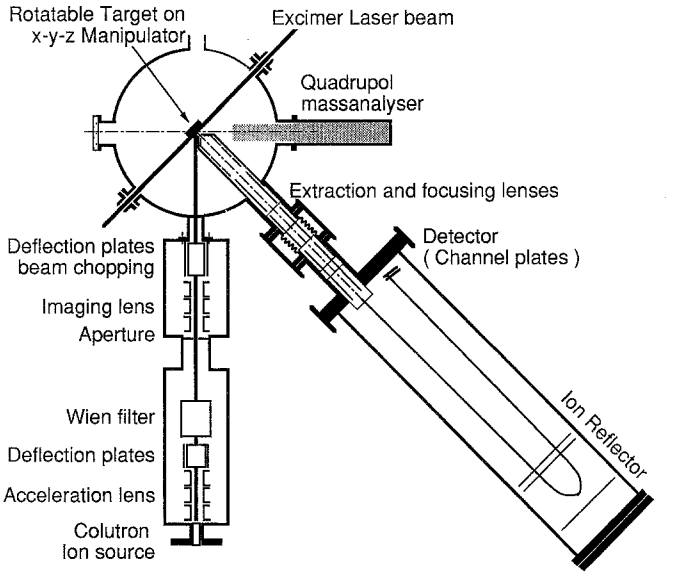

Fig. 2. Schematic of the Laser SNMS apparatus. A ion beam is used as probe beam. A energy focusing Time of Flight spectrometer is used for mass selective detection of the photo-ions

III Experimental results

The experimental data presented in this paper are *Clusters/Atoms*-ratios for Cu, Ag, Au and Cr obtained from SNMS measurement. Results are given for pure metal targets (Cu and Cr) and an AgCuAu alloy with known element concentrations (Ag:Cu:Au: 0.400:0.300:0.300). The corresponding results for 308 nm and 193 nm laser radiation for post-ionization are presented and compared.

In Fig. 3 the SNMS specta from an AgCuAu alloy with 193 nm and 308 nm laser radiation are compared. The obvious features of these results are the different cluster signals in the two spectra. In the lower part of the figure the case for 308 nm laser radiations is shown. In this situation Cu and Ag atoms can be ionized by two-photon absorption. However, three photons are needed to ionize the Au atoms.

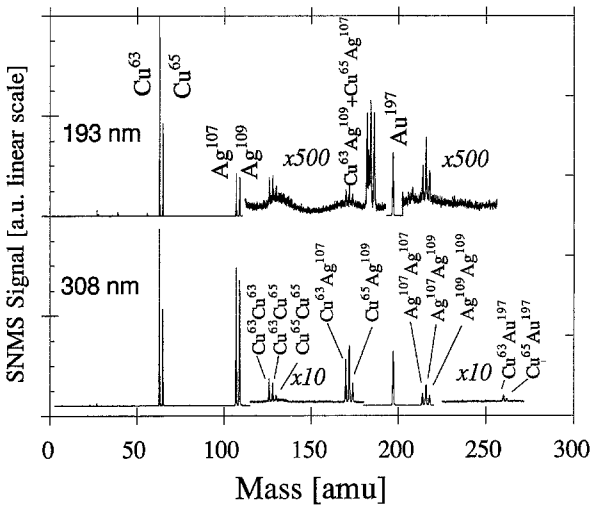

Fig. 3. SNMS spectra of an AgCuAu alloy (40%, 30%, 30%) obtained with 193 nm and 308 nm laser radiation for post-ionization. The x-axis is linear in arbitrary units. Some parts of the spectra are enlarged by factors given in the figure. The peak not labeled in the upper part of the figure is Pt

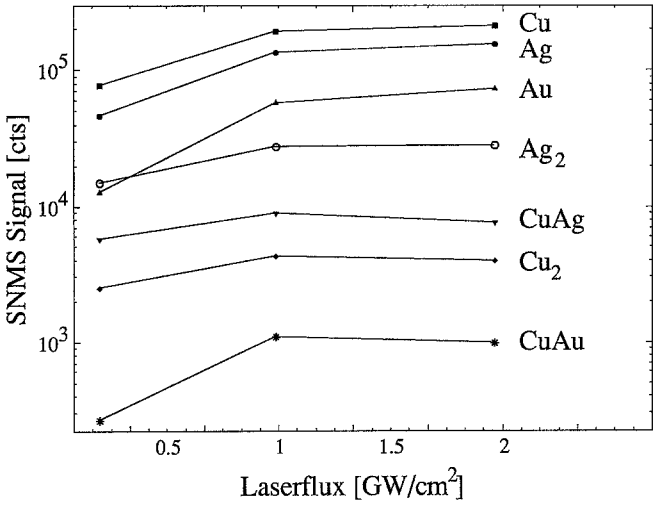

Fig. 4. Dependence of the SNMS signals on the laser flux

Therefore, the Au signal is considerably lower than the other signals and will not be used and discussed in detail in the following. The laser power has been adjusted to achieve saturation of the ionization of the Cu and Ag atoms. That this is indeed the case has been verified by measuring the photo-ion signal as a function of the laser power and is shown in Fig. 4. Because of the relative vicinity of transition lines from the groundstate of Ag (328 nm) and Cu (325 nm), efficient non-resonant ionization can be achieved. The absolute values given in Fig. 4 for the laser flux should be regarded with some reservation, because of the uncertainties in determining the actual size of the ionizing volume. We have measured the halfwidth of the laser beam in the focal region to be approximately 0.2×0.4 mm.

The cluster contributions are in fact quite substantial. If we look, for instance, at the numbers of copper atoms and clusters containing copper atoms, which are present in the sputtered flux, we find that the SNMS signals yield 86% Cu atoms, 4% Cu_2, 5.8% CuAg and 3.7% CuAu clusters. An even more dramatic effect is found for the corresponding Ag cluster contributions. Neglecting AgAu clusters, which have not been registered in our measurements, 78% are sputtered as Ag atoms, 16.3% as Ag_2 and 4.7 as CuAg clusters. The numbers given here represent number densities. If one is interested in flux ratios, one has to take into account the different energy distributions of monomers and dimers. As a general rule [17] the lower velocities of dimers result in reducing the dimer/atom-flux ratio by a factor of 2 as compared to the corresponding number density ratios.

We believe that the values given are good estimates for the lower limits of cluster contributions, because saturation of the atom ionization is close to unity and the clusters are ionized with probability one, as verified by power dependence measurements. However, for clusters, as outlined before, fragmentation of the clusters causes some uncertainty. In the power regime used, we observed a more or less constant cluster yield. The constant saturation behavior together with the relative high cluster signal makes us believe that cluster fragmentation does not play a too important role in this situation. We have also measured the cluster contributions from a Cu metal and obtained a value of 16 $\pm$ 2% as a lower limit. This correlates well with the results for the alloy, if one takes into account the stoichiometry of the sample (adding up all clusters containing a Cu atom and correcting for Ag-Au next neighbors).

The upper part of Fig. 3 shows the corresponding results obtained with 193 nm laser light for photo-ionization. Two things are notable. First, the copper signal dominates the Ag and Au (in this case two photons can ionize Au) signal. This can be attributed to insufficient saturation for the ionization of Ag and Au. For a quantitative analysis this has to be taken into account. We will be more concerned with the second aspect, that is the cluster contribution. Contrary to the case of 308 nm, only a "small cluster contribution is seen in the spectra". We attribute this to the fact, that evidently a substantial fragmentation takes place for 193 nm ionization. This becomes even more clear, if one investigates the laser power dependence of the cluster yield from a Cu metal target. By decreasing the laser power by a factor of 40 from the maximum value, the Cu signal is constant in most of the power regime and then drops by a factor of 2. On the other hand, the low Cu-dimer signal increases by more than one order of magnitude for decreasing the laser power by a factor of 10 before it starts dropping again in the low end of the power regime. In fact, it exhibits the general behavior discussed in Fig. 1. Here, the maximum of the "measured" cluster contribution is below 1% of the Cu-monomer contribution. A trimer signal, again about one order of magnitude lower than the dimer signal, has also been found.

An opposite situation is encountered for Cr, as shown in Fig. 5. In this case absolutely no clusters are found using 308 nm, but a high cluster contribution of 10% is detected using 193 nm light for post-ionization. The cluster contribution was determined by integrating the peaks of the Cr isotopes and Cr-dimer isotopes, respectively. (The integration was actually not performed on the mass axis but on the corresponding time axis.) Variation of the laser power by a factor of 10 resulted in practically no change of the Cr as well as the Cr dimer signal. This can be taken as an indication, that saturation is indeed achieved and fragmentation plays a minor role in this case.

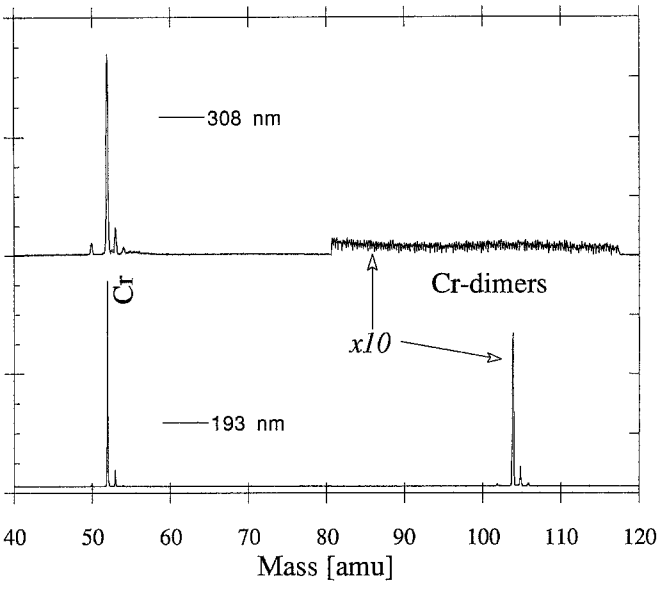

Fig. 5. SNMS spectra of Cr obtained with 193 nm and 308 nm laser radiation for post-ionization. The y-axis is linear in arbitrary units. The cluster-signal is enlarged by a factor of 10

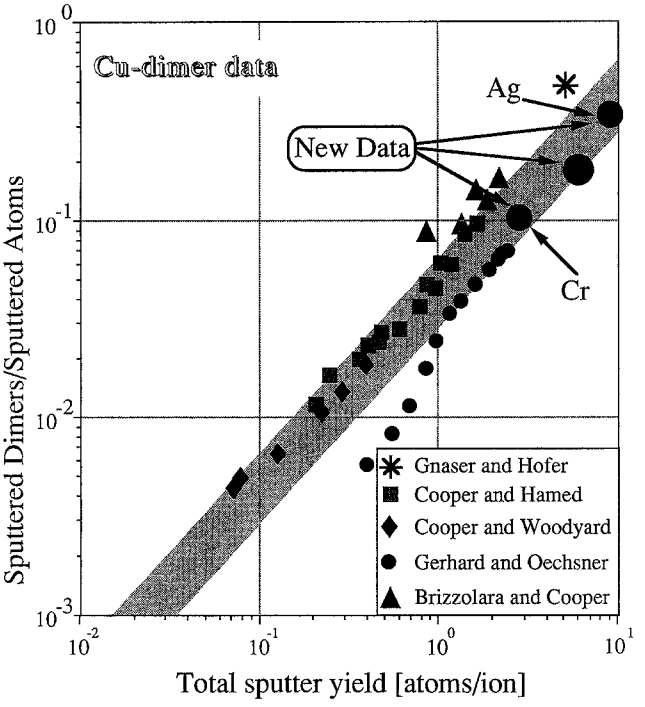

Fig. 6. The number density ratios of sputtered dimers to sputtered atoms versus the sputter yield is shown for Cu. Our new data for Cu, Ag and Cr are compared with existing Cu data from the literature in the energy range from 50 to 90 eV [16], from [2] in the energy range from 100 to 1000 eV and in the energy range from 60 to 300 eV [3]. A linear fit through the data points in double logarithmic representation demonstrates the general trend

IV Discussion and conclusions

The measurements presented in the previous chapter demonstrate that cluster contribution can be quite a substantial factor in the flux of secondary particles under ion bombardment of solids. Furthermore, from the measurements presented it becomes clear, that it depends quite dramatically on the experimental parameters, whether the cluster can be actually identified or not. Even restricting ourselves to SNMS using laser post-ionization, large discrepancies can be seen depending on the laser wavelength, laser power and target material.

Measured absolute *Sputtered Dimers/Sputtered Atoms* ratios have to be regarded with care, if they are obtained uniquely with one experimental method under identical conditions. If the measurements can be performed with different methods and/or the results can be cross-checked by varying the ionizing radiation with respect to energy (wavelength) and intensity, it is possible to obtain lower limits for absolute *Sputtered Dimers/Sputtered Atoms* ratios. Furthermore, saturation should be achieved and fragmentation should minimized. Otherwise the experimental results are unreliable.

Under these conditions it makes sense to plot the *Sputtered Dimers/Sputterd Atoms* ratios as a function of the sputter yield, which is known for many materials and ion bombarding energies and was obtained in our case from the tables by Matsunami et al. [15]. For this purpose we have taken copper data from the literature (employing plasma or electron beam post-ionization) [2–4, 16, 17] for Cu obtained for different ion beam energies and plotted the ratios as a function of the sputter yield in double-logarithmic form (Fig. 6). The recombination mechanism for cluster formation [8] then would predict a straight line for the dependence. Our data for *Secondary Cluster/Secondary Atoms* ratios are added to the figure and fit very well into the proposed dependence on the sputter yield. We would like to emphasize that the figure should be merely used for the demonstration of a general trend. The values shown are from different authors and have been obtained under various conditions, and, therefore, cannot be regarded as absolute numbers.

Furthermore, we have added the data for Cr and Ag to the figure. The different sputter yields at 8 keV Ar^+ bombardment of Cr, Cu and Ag were taken into account. Within the limits of the experimental error the validity of our assumptions seem to be verified and a correlation between the sputter yield and the *Sputter Dimers/Sputtered Atoms* ratios can be established.

This is in contradiction to conclusions in [4] where it is argued that the "low" cluster, but high sputter yield of Zn is a reason for rejecting the idea of correlating the cluster ratio to the sputter yield. This might be caused by a too low measured cluster contribution due to the reasons mentioned above, but a dependence of the cluster ratio on the electronic configuration of the material cannot be excluded. However, in the cases presented in this paper (Cu, Ag, Au, Cr) no such dependence has been found and the cluster yields seem to depend simply on the density of sputtered secondaries. A further indication for this is also the fact, that the cluster yield for Cu from the metal and the alloy is solely governed by the stoichiometry of the sample.

The relevance for analytical laser SNMS can be demonstrated with the results of the AgCuAu alloy. Due to the saturation of Cu and Ag ionization with 308 nm laser light the concentration of the different elements (excluding Au) can be obtained directly from the SNMS signals without using standards. This is, however, only true if the cluster contributions are taken into account. One then obtains for

the Ag-concentration 0.38 ± 0.02 and for the Cu concentration 0.32 ± 0.02 in good agreement with the known standard values 0.400 and 0.300.

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